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Optical free induction decay of molecules undergoing radiative and radiationless relaxation

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In this paper we examine the effect of radiative and radiationless processes on optical free induction decay (OFID) in singlet–singlet transitions of molecules in the condensed phase. The main conclusion is that the applicability of OFID to molecular singlet–singlet transitions is severely limited by the presence of an intermediate triplet state, which quite often forms a bottleneck in the optical pumping cycle. Using the theoretically derived formulas for the OFID signal, we examine the feasibility of OFID experiments on the mixed crystals of porphin in *n*-octane and naphthalene in durene and conclude that such experiments, if at all fruitful, would be difficult to execute. We re-evaluate the reported OFID results of pentacene in *p*-terphenyl and obtain for the lowest $^1B_{2u} \leftarrow {}^1A_{1g}$ transition a dipole moment of 0.9 ± 0.3 D.

I. INTRODUCTION

A few years ago, optical free induction decay (OFID) became available as a new method for studying optical dephasing processes (T_2 processes, where T_2 is the transverse relaxation time in the optical analog of the Bloch equations). While the original technique employing Stark switching of the molecular transition[1] was limited to the study of polar molecules, the cw dye laser switching technique recently introduced by Brewer and Genack[2] can be used to study *any* optical transition. This new tool to observe coherent optical phenomena is therefore expected to play an important role in the field of molecular spectroscopy.

So far with this new technique OFID has been studied for I_2 in the gas phase[2] and in a molecular beam,[3] and for the systems Pr^{3+}/LaF_3[4] and pentacene in *p*-terphenyl.[5] With regard to the analysis of the OFID signals obtained in these systems, only a theoretical formula derived for two-level systems[1,6,7] has been used (except in Ref. 5). The aforementioned systems and most of future interest are clearly not simple two-level systems as was demonstrated by Genack, Macfarlane, and Brewer[4] in the case of the system Pr^{3+}/LaF_3.

Schenzle and Brewer[8] have recently treated a two-level system in contact with a general multilevel reservoir and obtained formal solutions for most optical coherent transients. In the Schenzle–Brewer model, the reservoir levels are assumed to exist in thermal equilibrium and the effect of optical excitation on the population distribution in the reservoir is ignored. The effect of these assumptions manifests itself in the final result for $\tilde{\rho}_{12}(t)$ in OFID, which still contains diagonal elements of the density matrix for the intermediate levels.

In this paper the above-mentioned assumptions are not made and the density matrix equations are solved for the steady state situation. The final result obtained for $\tilde{\rho}_{12}(t)$ is similar, though not identical, to that of Schenzle and Brewer. We further restrict ourselves to a model system that specifically applies to $S_1 - S_0$ transitions of molecules in the condensed phase at low temperatures. Extension to an *n*-level system however is trivially made.

II. OFID IN $S_1 \leftarrow S_0$ TRANSITIONS OF MOLECULES IN MIXED CRYSTALS

A. The low temperature limit

In the following we derive a formula for the OFID $1/e$ decay time (τ_{OFID}) of the model system shown in Fig. 1. $|1\rangle$ is the singlet ground state, $|2\rangle$ the vibrationless lowest excited singlet state, and $|3x\rangle$, $|3y\rangle$, and $|3z\rangle$ are the spin components of the vibrationless lowest triplet state. Level $|2\rangle$ decays radiatively (rate constant $k_{21}^{(r)}$) and radiationlessly ($k_{21}^{(nr)}$) to the ground state but only radiationlessly to the triplet state manifold ($k_{23}^{x,y,z}$). The triplet state spin-sublevels themselves decay both radiatively ($k_{31}^{(r)x,y,z}$) and radiationlessly ($k_{31}^{(nr)x,y,z}$) to the ground state. By the low temperature limit we mean that the effect of spin–lattice relaxation on the OFID is negligible.

We assume then that for all molecules the local radiation field

$$E_x(z,t) = E_0 \cos(\Omega t - kz) \tag{1}$$

has frequency Ω and amplitude E_0, is polarized along the x direction (which is taken to be parallel to the electric dipole transition moment μ_{12}), and propagates in the z direction. This field only couples levels $|1\rangle$ and $|2\rangle$. For the time derivative of the nondiagonal element ρ_{12} of the density matrix we can write[9]

$$\dot{\rho}_{12} = \left(-\frac{1}{T_2} + i\omega\right)\rho_{12} - \frac{iV_{12}}{\hbar}\,(\rho_{22} - \rho_{11}) \quad , \tag{2}$$

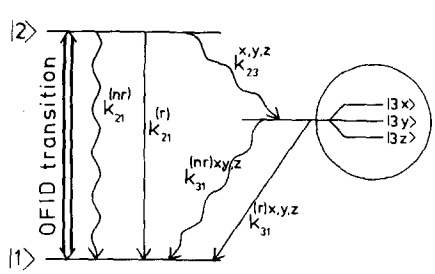

FIG. 1. Molecular model system. The meaning of the energy levels is discussed in the text. Straight and wavy arrows indicate radiative and radiationless transitions, respectively. The part within the circle has a greatly magnified ($\sim 10^4$) energy scale.

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where $\omega = \omega_2 - \omega_1$ and the decay rate $1/T_2$ has been introduced phenomenologically. $V_{12} = -\mu_{12} E_0 \cos(\Omega t - kz)$ is the matrix element of the perturbative coupling between molecule and field.

Introducing the rotating wave approximation by putting

$$\frac{V_{12}}{\hbar} = -\frac{\mu_{12} E_0}{2\hbar} e^{i(\Omega t - kz)} \equiv -\tfrac{1}{2}\chi e^{i(\Omega t - kz)} \tag{3}$$

and $\rho_{12} = \tilde{\rho}_{12} e^{i(\Omega t - kz)}$ we get

$$\dot{\tilde{\rho}}_{12} = \left(-\frac{1}{T_2} + i\Delta\right)\tilde{\rho}_{12} + \tfrac{1}{2} i\chi(\rho_{22} - \rho_{11}) , \tag{4}$$

where $\Delta = \omega - \Omega$. The OFID beat signal is proportional to $\tilde{\rho}_{12}$ averaged over the entire inhomogeneous width of the transition, written as $\langle \tilde{\rho}_{12} \rangle$.[7] During the preparation before the laser frequency switch, $\tilde{\rho}_{12}$ reaches its steady state value $\tilde{\rho}_{12}(\infty)$. After the moment of switching, which is taken as a new origin of time, the molecules prepared at $t < 0$ radiate freely, and for these molecules we obtain from (4)

$$\tilde{\rho}_{12}(t) = \tilde{\rho}_{12}(\infty) e^{(-1/T_2 + i\Delta)t} . \tag{5}$$

Thus our first task is to calculate $\tilde{\rho}_{12}(\infty)$.

Denoting the transition rate from level $|n\rangle$ to $|m\rangle$ by k_{nm}, we write down the equations of motion for the diagonal elements of the density matrix:

$$\dot{\rho}_{11} = k_{21}\rho_{22} + k_{31}^x \rho_{33}^x + k_{31}^y \rho_{33}^y + k_{31}^z \rho_{33}^z + \tfrac{1}{2} i\chi(\tilde{\rho}_{21} - \tilde{\rho}_{12}) \tag{6}$$

$$\dot{\rho}_{22} = -(k_{21} + k_{23}^x + k_{23}^y + k_{23}^z)\rho_{22} + \tfrac{1}{2} i\chi(\tilde{\rho}_{12} - \tilde{\rho}_{21}) , \tag{7}$$

$$\dot{\rho}_{33}^x = k_{23}^x \rho_{22} - k_{31}^x \rho_{33}^x , \tag{8}$$

$$\dot{\rho}_{33}^y = k_{23}^y \rho_{22} - k_{31}^y \rho_{33}^y , \tag{9}$$

$$\dot{\rho}_{33}^z = k_{23}^z \rho_{22} - k_{31}^z \rho_{33}^z . \tag{10}$$

Here k_{21}, $k_{31}^{x,y,z}$ are the sums of the respective radiationless ($k_{nm}^{(nr)}$) and radiative ($k_{nm}^{(r)}$) decay rates. All the off-diagonal elements ρ_{nm} remain zero in this case except ρ_{12} and ρ_{21}. We now have to find the steady state solutions for the density matrix elements.

It follows from (4) and (6) through (10) that we may write down the following relations:

$$\dot{\rho}_{11} = 0 = K_2 \rho_{22} + \tfrac{1}{2} i\chi(\tilde{\rho}_{21} - \tilde{\rho}_{12}) , \tag{11}$$

$$\dot{\rho}_{22} = 0 = -K_2 \rho_{22} + \tfrac{1}{2} i\chi(\tilde{\rho}_{12} - \tilde{\rho}_{21}) , \tag{12}$$

$$\dot{\tilde{\rho}}_{12} = 0 = \left(-\frac{1}{T_2} + i\Delta\right)\tilde{\rho}_{12} + \tfrac{1}{2} i\chi(\rho_{22} - \rho_{11}) , \tag{13}$$

where $K_2 = k_{21} + k_{23}^x + k_{23}^y + k_{23}^z$. In addition we have $\sum_i \rho_{ii} = 1$ or

$$\rho_{11} = 1 - \rho_{22}(1 + A) , \tag{14}$$

where $A = k_{23}^x/k_{31}^x + k_{23}^y/k_{31}^y + k_{23}^z/k_{31}^z$.

Calculating $\tilde{\rho}_{12}(\infty)$ from (12), (13), and (14) and substituting it into (5) we obtain

$$\tilde{\rho}_{12}(t) = -\frac{\chi}{2} \frac{(i/T_2 - \Delta)}{\Delta^2 + 1/T_2^2 + \hat{K}^2} e^{(-1/T_2 + i\Delta)t} , \tag{15}$$

where

$$\hat{K}^2 = \frac{\chi^2 (1/T_2)}{2K_2}(2 + A) .$$

Finally we get the following integral over the inhomogeneous line which we take to be Gaussian with central frequency ω_0 and fwhm $\Delta\omega_G$,

$$\int_{-\infty}^{+\infty} \exp\left[-\left(\frac{2\sqrt{\ln 2}(\omega - \omega_0)}{\Delta\omega_G}\right)^2\right] \frac{(i/T_2 - \Delta)}{\Delta^2 + 1/T_2^2 + \hat{K}^2} e^{(-1/T_2 + i\Delta)t} d\omega . \tag{16}$$

We consider the case where $\Delta\omega_G$ far exceeds the homogeneous linewidth of the $|1\rangle - |2\rangle$ transition. Assuming that only a small fraction of the inhomogeneous line is excited, one can take the Gaussian outside the integral. This approximation should not be made if one is interested in the onset of the OFID signal during a time of the order $2\sqrt{\ln 2}/\Delta\omega_G$ after the laser frequency switch, as was pointed out by Foster, Stenholm, and Brewer[7] (see also Ref. 10). In the case of pentacene in p-terphenyl, for example, this amounts to about 10 psec, which is very much shorter than the low temperature T_2 of 43 nsec.[5] We now proceed and solve the remaining integral by contour integration. We obtain for $\langle \tilde{\rho}_{12}(t) \rangle$:

$$\langle \tilde{\rho}_{12}(t) \rangle = \frac{i\pi\chi}{2} \exp\left[-\left(\frac{2\sqrt{\ln 2}(\Omega - \omega_0)}{\Delta\omega_G}\right)^2\right] \times \left\{1 - \frac{1/T_2}{\sqrt{1/T_2^2 + \hat{K}^2}}\right\} \exp\left[-\left(\frac{1}{T_2} + \sqrt{\frac{1}{T_2^2} + \hat{K}^2}\right)t\right] . \tag{17}$$

The OFID decay rate then becomes

$$\frac{1}{\tau_{OFID}} = \frac{1}{T_2}\left[1 + \sqrt{1 + \frac{\mu_{12}^2 E_0^2}{\hbar^2} \frac{T_2}{2K_2}(2 + A)}\right] , \tag{18}$$

whereby $K_2 = k_{21} + k_{23}^x + k_{23}^y + k_{23}^z$ and

$$A = \frac{k_{23}^x}{k_{31}^x} + \frac{k_{23}^y}{k_{31}^y} + \frac{k_{23}^z}{k_{31}^z} .$$

Note that the results (17) and (18) are insensitive to the number of levels lying in between $|1\rangle$ and $|2\rangle$. For n intermediate levels K_2 contains $(n+1)$ relaxation rates and A is a sum of n ratios of rates.

We further wish to emphasize that Eq. (17) is similar, though not identical, to Eq. (4.24) of the Schenzle–Brewer paper.[8] First note that $\tilde{\rho}_{12}(t)$ of Eq. (17) contains no diagonal elements of the density matrix as Eq. (4.24) does. Also note that $\hat{K}^2$, to be compared with $\hat{\Gamma}^2$ of Eq. (4.24), contains a sum of ratios of populating and decay constants, while $\hat{\Gamma}^2$ contains a ratio of sums of these constants.

We also note that, when $K_2 = k_{21} \equiv 1/T_1$ and A is zero, Eq. (18) reduces to the well-known two-level OFID decay formula.[1,6]

We finally remark that inclusion of very fast relaxing ground state vibrational levels merely adds negligible terms to the quantity A.

B. The effect of spin–lattice relaxation

In molecular mixed crystals at liquid helium temperature spin–lattice relaxation rates often are no longer negligible compared to the populating and decay rates k_{23} and k_{31}. We then obtain instead of Eqs. (8), (9), and (10),

$$\dot{\rho}^x_{33} = k^x_{23}\rho_{22} - k^x_{31}\rho^x_{33} - k_{xy}\rho^x_{33} - k_{xz}\rho^x_{33} + k_{yx}\rho^y_{33} + k_{zx}\rho^z_{33}\,, \tag{19}$$

and similar equations for $\dot{\rho}^y_{33}$ and $\dot{\rho}^z_{33}$. Here k_{xz} denotes the rate constant for the lattice induced transition $|3x\rangle \rightarrow |3z\rangle$, etc. The steady state treatment in this case again yields the τ_{OFID} formula (18). But in contrast with the low temperature limit, the quantity A now becomes in general a complicated function of the 12 rate constants which determine feeding and decay of the triplet level system. At this point we want to emphasize that the power term in the OFID decay formula is temperature dependent. Thus when performing a temperature dependent T_2 study, it is necessary to extrapolate τ_{OFID} to zero laser power at *every* temperature.

C. Pseudo-three-level systems

When, in the low temperature limit, population of the triplet state only occurs into one of its spin sublevels, the system can be considered as a pseudo-three-level system with rate constants k_{23} and k_{31}.

Equation (18) then becomes

$$\frac{1}{\tau_{OFID}} = \frac{1}{T_2}\left[1 + \sqrt{1 + \frac{\mu_{12}^2 E_0^2}{\hbar^2}\,\frac{T_2\tau_{fl}}{2}\left(\frac{2k_{31}+k_{23}}{k_{31}}\right)}\right]\,, \tag{20}$$

which is equivalent to the formula stated in Ref. 5.

When spin–lattice relaxation is fast compared to the populating and decay rates $k^{x,y,z}_{23}$ and $k^{x,y,z}_{31}$, Formula (20) also applies, where k_{23} and k_{31} are the appropriate average rate constants. Of course with continuous microwave radiation in two of the transitions between spin sublevels, one creates also a pseudo-three-level system.[11]

D. The effect of phonon scattering

To examine the effect of phonon scattering we add to the scheme of Fig. 1 the levels $|4\rangle$, $|5\rangle$, and $|6x,y,z\rangle$ (lying ~ 10–20 cm^{-1} above $|1\rangle$, $|2\rangle$, and $|3x,y,z\rangle$, respectively). These levels are meant to be pseudolocalized phonon levels. Recent photon-echo[12–15] and photochemical hole-burning[16] experiments seem to indicate that such phonon levels play an important part in the dephasing of electronically excited molecules in the condensed phase.

We only consider population and decay of these levels from and to their respective pure electronic states. The formalism of Sec. II.A yields in this case a formula similar to (17) except for an additional pre-exponential factor $1/(1+B)$, while $\hat{K}^2$ is now defined as $[\chi^2(1/T_2)/2K_2][1+(1+A)/(1+B)]$. Here $B = k_{14}/k_{41}$, while A, in general, is a complicated function of the feeding and decay rates to, from, and within the $|3x,y,z\rangle$, $|6x,y,z\rangle$ triplet level system.

Note that in the present case we still have $K_2 = k_{21} + k^x_{23} + k^y_{23} + k^z_{23}$; however, $K_2 \neq 1/\tau_{fl}$!

We finally want to emphasize that coherence transfer processes[17–19] have been excluded in the present treatment.

E. Discussion

The following comments on the theoretical results obtained thus far seem appropriate.

First note that, as in the Schenzle–Brewer model,[8] T_2 may be obtained from an OFID experiment when τ_{OFID} is extrapolated to zero laser power. Closely related to this point is the notion that the transition dipole moment (μ_{12}) cannot be determined unless all relevant relaxation constants are known.

We further wish to emphasize that hyperfine levels of paramagnetic states that participate in the optical pumping cycle play a role[4,20] similar to the triplet state levels of Fig. 1. The theory is also applicable to OFID experiments on molecules in the low pressure gasphase. In this case the vibrational levels may cause a considerable contribution to the quantity A as vibrational relaxation rates are no longer much greater than the other decay rates.

Application of the theory in the next section to some molecular mixed crystals at low temperature shows that the intermediate triplet state may seriously limit the applicability of the OFID technique, as it may act as a bottleneck in the pumping cycle.

III. APPLICATIONS

As an example we discuss the feasibility of an OFID experiment on the lowest $S_1 - S_0$ transition of free base porphin in n-octane in the low temperature limit.

Based upon our experience with OFID in molecular mixed crystals, we would require, in order to obtain reliable T_2 results: $\tau_{OFID} \gtrsim T_2/4$,[5] or using (18):

$$\frac{\mu_{12}^2 E_0^2}{\hbar^2}\,\frac{T_2}{2K_2}\,(2+A) \lesssim 8\,. \tag{21}$$

We now want to make an estimate of the laser power that should be used. At low temperature T_2 is completely determined by the fluorescence lifetime as was measured by photochemical hole burning,[18] giving $T_2 = 2\tau_{fl} = 34$ nsec. The quantity K_2 is just $1/\tau_{fl}$ here and thus equal to 5.9×10^7 sec^{-1}. We calculate μ_{12}^2 as follows. From the fluorescence lifetime and quantum yield (0.05)[21] we obtain a radiative lifetime of the S_1 state of 340 nsec. From this value a total oscillator strength $f = 1.6\times10^{-2}$ can be calculated. Estimating that about 1% of this strength is carried by the 0–0 transition,[22] we obtain $\mu_{12}^2 = 0.21\times10^{-60}$ $C^2m^2 = 1.9\times10^{-2}$ D^2. We now determine A. As we can assume $S_0 - S_1$ internal conversion to be negligible,[21] we have $K_2 = k_{21}^{(r)} + k_{23}^{total}$, giving $k_{23}^{total} = 5.6\times10^7$ sec^{-1}. Combining this with the known populating probabilities and decay rates of the triplet spin sublevels levels, reported in Ref. 11, the quantity A becomes 4.9×10^5.

In order to meet Condition (21) we obtain $E_0^2 \lesssim 3.0\times10^3$ V^2/m^2. Here the laser is assumed to be polarized parallel to the dipole moment direction. Then, performing an OFID experiment on the $S_1 - S_0$ transition in porphin in n-octane at 1.3 K, one should use a laser power $I \lesssim 4.0\times10^{-3}$ mW/mm^2 (assuming the local electric field to be of the order of the laser field). There-

fore, comparing the porphin example with the case of pentacene in p-terphenyl,[5] one would like to increase the sensitivity of the detection about a hundredfold. Note here that the feasibility of this porphin experiment will not be greater for another μ_{12} value of the $S_1 \leftarrow S_0$ transition, as both τ_{OFID} and the OFID beat amplitude depend on $\mu_{12}^2 E_0^2$.

The influence of the indirectly coupled levels on the OFID signal is also evident when, in the porphin case, we had simply considered the two-level OFID formula. Then Condition (21) with A equal to zero would have yielded $I \lesssim 9.7 \times 10^2$ mW/mm^2. Thus, compared to the two-level case with the same transition moment, the experimental maximum intensity really required is smaller by a factor of 2.4×10^5, which means that the detected OFID beat signal amplitude is also diminished by this factor.

Considering the OFID decay time the effect of the indirectly coupled levels again becomes very clear in the porphin example. Using $I = 0.5$ mW/mm^2 to obtain a conveniently measurable signal amplitude, we calculate from (18): $\tau_{OFID} = T_2/33 = 1.0$ nsec. Extrapolation of τ_{OFID} from measurements in this power range would not yield a very reliable T_2 value, but moreover the applicability of intracavity-switched OFID is doubtful when $\tau_{OFID} \lesssim 3$ nsec (laser cavity round-trip time).[23]

It may be interesting to make a comparison here with the pentacene case, where an easily measurable OFID signal yields a reliable T_2 value using a laser power varying around 0.4 mW/mm^2.[5] Applying the theory of Sec. II.A and using the experimental data available at present, we will re-evaluate these OFID results. With a power on the crystal of 0.2 mW/mm^2 we measured, on the energetically lowest site of pentacene in a low temperature p-terphenyl crystal, $\tau_{OFID} = 18$ nsec, while extrapolating τ_{OFID} to zero laser power yields $T_2 = 43$ nsec. As the fluorescence lifetime of pentacene in p-terphenyl for this site was measured to be 23.5 nsec,[14] we obtain $K_2 = 1/\tau_{fl} = 4.26 \times 10^7$ sec^{-1}. Assuming $E_0^b = 1.78\, E_{laser}$,[24] we have for $I = 0.2$ mW/mm^2: $E_0^2 = 4.8 \times 10^5$ V^2/m^2. We now obtain from (18): $\mu_{12}^2(2+A) = 4.3 \times 10^{-59}$ C^{2}m^2. Very recently the populating probabilities and decay rates of the triplet spin sublevels of pentacene in p-terphenyl at 77 K have been determined.[25] As the intersystem crossing yield ($|3\rangle \leftarrow |2\rangle$) for this site was also recently determined to be 0.003,[26] we conclude that $\mu_{12}^2 = 0.55$ D^2. As in the pentacene OFID experiment the laser was polarized parallel to the crystal b axis, we have for the molecular transition dipole moment $\mu(^1B_{2u} \leftarrow {}^1A_{1g}) = 1.21\ \mu_{12}$,[24] or $\mu = 0.9 \pm 0.3$ D. A 0.3% intersystem crossing yield means that $A \approx 5$; in pentacene, which is smaller than the A value of porphin by a factor of about 10^4. This is caused by a $\sim 10^2$ times larger triplet depletion rate k_{31} for pentacene and a $\sim 10^2$ times smaller intersystem crossing rate k_{23}^{total} as compared to porphin in n-octane.

At this point we want to emphasize the importance of the quantities $\mu_{12} E_0$ and A in regard of the feasibility of OFID experiments on molecular $S_1 \leftarrow S_0$ transitions. $\mu_{12} E_0$ (Rabi frequency times $\hbar$) has to meet two opposing conditions. Firstly, it has to be small enough to ensure the OFID decay to be determined mainly by T_2 [Condition (21)]. Secondly, it has to be large enough to ensure a measurable OFID signal amplitude, as this is nearly proportional to $\mu_{12}^2 E_0^2$.[6,7] The importance of the quantity A in the OFID power term is its ability to make the two conditions for $\mu_{12} E_0$ incompatible. Therefore a smaller intersystem crossing rate k_{23} (smaller quantum yield for intersystem crossing) and a larger triplet depletion rate k_{31}, both resulting in a smaller A value, enhance the possibility for $S_1 \leftarrow S_0$ OFID experiments.

As another example we calculated, using available data,[15,27-30] the feasibility, in the low temperature limit, of an $S_1 \leftarrow S_0$ OFID experiment on naphthalene in a durene mixed crystal. Using, for example, a laser power of about 150 mW/mm^2, to obtain a conveniently measurable OFID signal amplitude, we find from formula (18): $\tau_{OFID} = T_2/3465 = 46$ psec (where T_2 is taken to be 160 nsec).[15] It can be concluded that for this molecule the $S_1 \leftarrow S_0$ OFID experiment seems out of reach.

In conclusion of this section an additional experimental possibility should be discussed. Considering the examples of porphin and naphthalene, one would like to use more laser power than calculated above from Condition (21), while maintaining a value for τ_{OFID} mainly determined by T_2. The question arises if this could be accomplished by sweeping the laser frequency (velocity $d\Omega/dt$) during the OFID experiment. This sweeping OFID technique was first applied by Genack, Macfarlane, and Brewer to overcome the bottleneck problem in the system Pr^{3+}/LaF_3.[4] In order to use this technique fruitfully one would require $\chi^2,\ k_{23}^2 \ll d\Omega/dt \ll 1/T_2^2$.[4] For the cases of porphin, pentacene, and naphthalene discussed above the value of $1/T_2^2$ is of the order of 10^{14} sec^{-2}, while for the single frequency cw dye lasers commercially available at present $d\Omega/dt \lesssim 4 \times 10^{11}$ sec^{-2}. With the highest sweep rate thus available the condition $d\Omega/dt \ll 1/T_2^2$ is therefore fulfilled for the molecules discussed. The other requirement now amounts to $\chi^2,\ k_{23}^2 \ll 4 \times 10^{11}$ sec^{-2}. For porphin this requirement cannot be met as $k_{23}^2 = 3.1 \times 10^{15}$ sec^{-2}, and the same is true for naphthalene where $k_{23}^2 = 2.6 \times 10^{13}$ sec^{-2}. Moreover, calculating for the cases of porphin and naphthalene, the laser power that should be used to meet the condition $\chi^2 \ll 4 \times 10^{11}$ sec^{-2}, it follows that the respective OFID signal amplitudes would still be very difficult to detect. For pentacene the situation would be more profitable as here $k_{23}^2 = 1.6 \times 10^{10}$ sec^{-2}, but in this case the OFID experiment is already possible without sweeping the laser frequency.

We conclude here that for the cases discussed, sweeping the frequency of the laser does not improve the applicability of OFID.

IV. FINAL REMARKS

While the feasibility of the OFID method in the study of dephasing of $S_1 \leftarrow S_0$ excited molecules was theoretically demonstrated in Sec. II, the serious practical limitations were illustrated in Sec. III.

In this section a physical picture will be given of the effects discussed in the preceding sections. In addition

attention will be paid to possible limitations of the intracavity-switched OFID technique.

Consider the buildup of population in other levels than $|1\rangle$ and $|2\rangle$. This causes enhanced hole burning in the inhomogeneously broadened $|2\rangle \leftarrow |1\rangle$ transition. When these intermediate levels have decay times long compared to τ_{fl}, they form a bottleneck in the optical pumping cycle. This may seriously limit the repetition rate in possible OFID[4] as well as in photon-echo experiments.[15] We note here that with low enough repetition rates the photon echo, in contrast to OFID, is not affected by the bottleneck. A second point we want to emphasize, considering OFID, is the importance of the relation that exists between the homogeneous width $1/\pi T_2$ of the transition studied, the degree of off-resonance pumping, and the range of laser frequency jitter during a time of the order of T_2. So far we have assumed in our treatment the laser frequency jitter, during a period of time T_2, to be negligible compared to the frequency width $1/\pi T_2$.

Then, as a result of the population buildup mentioned above, the power term in the OFID decay formula can be greatly enhanced as shown in Sec. III. This can physically be reasoned as follows. The additional hole burning results in more intense off-resonance pumping, thus making the inhomogeneous part of the OFID decay more important; in other words, the signal will decay faster. When $\tau_{OFID} \lesssim 3$ nsec, the applicability of the intracavity-switched OFID method is doubtful,[23] as already mentioned in Sec. III.

Now assume that laser frequency jitter during a time of the order T_2 is comparable with the homogeneous linewidth. Then, after the moment of switching we get OFID signals from subensembles of molecules with different transition frequencies that were coherently excited consecutively during a period of time of the order T_2 just before the frequency-switch. Therefore the decay of the detected OFID beat signal will not only be determined by T_2 and the degree of off-resonance pumping but also by the range of laser frequency jitter during a period of the order of T_2. When this frequency jitter far exceeds the width $1/\pi T_2$, off-resonance pumping will become negligible as the preparation time of a certain subensemble will be short compared to the Rabi period. In these circumstances the OFID signal decay will be completely determined by the frequency jitter range. Without frequency stabilization one would be limited to measurement of T_2's in the range of $T_2 \lesssim 10$ μsec.[31,32]

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[1]R. G. Brewer and R. L. Shoemaker, Phys. Rev. Lett. 27, 631 (1971); Phys. Rev. A 6, 2001 (1972).
[2]R. G. Brewer and A. Z. Genack, Phys. Rev. Lett. 36, 959 (1976).
[3]A. H. Zewail, T. E. Orlowski, R. R. Shah, and K. E. Jones, Chem. Phys. Lett. 49, 520 (1977).
[4]A. Z. Genack, R. M. Macfarlane, and R. G. Brewer, Phys. Rev. Lett. 37, 1078 (1976).
[5]H. de Vries, P. de Bree, and D. A. Wiersma, Chem. Phys. Lett. 52, 399 (1977).
[6]F. A. Hopf, R. F. Shea, and M. O. Scully, Phys. Rev. A 7, 2105 (1973).
[7]K. L. Foster, S. Stenholm, and R. G. Brewer, Phys. Rev. A 10, 2318 (1974).
[8]A. Schenzle and R. G. Brewer, Phys. Rev. A 14, 1756 (1976).
[9]M. Sargent III, M. O. Scully, and W. E. Lamb, Jr., *Laser Physics* (Addison-Wesley, Reading, MA, 1974), Chap. 7.
[10]J. R. R. Leite, R. L. Sheffield, M. Ducloy, R. D. Sharma, and M. S. Feld, Phys. Rev. A 14, 1151 (1976).
[11]W. G. van Dorp, W. H. Schoemaker, M. Soma, and J. H. van der Waals, Mol. Phys. 30, 1701 (1975).
[12]T. J. Aartsma and D. A. Wiersma, Chem. Phys. Lett. 42, 520 (1976).
[13]T. J. Aartsma, J. Morsink, and D. A. Wiersma, Chem. Phys. Lett. 47, 425 (1977).
[14]J. B. W. Morsink, T. J. Aartsma, and D. A. Wiersma, Chem. Phys. Lett. 49, 34 (1977).
[15]T. J. Aartsma and D. A. Wiersma, Chem. Phys. Lett. 54, 415 (1978).
[16]S. Völker, R. M. Macfarlane, A. Z. Genack, H. P. Trommsdorff, and J. H. van der Waals, J. Chem. Phys. 67, 1759 (1977).
[17]S. Stenholm, J. Phys. B 10, 761 (1977).
[18]C. A. van't Hoff and J. Schmidt, Chem. Phys. Lett. 36, 460 (1975).
[19]C. B. Harris, J. Chem. Phys. 67, 5607 (1977).
[20]W. H. Hesselink and D. A. Wiersma, Chem. Phys. Lett. 50, 51 (1977).
[21]A. T. Gradyushko and M. P. Tsvirko, Opt. Spectrosc. 31, 291 (1971).
[22]W. G. van Dorp, thesis, University of Leiden, 1975.
[23]A. Z. Genack and R. G. Brewer, Phys. Rev. A 17, 1463 (1978). In this τ_{OFID}-range laser oscillation in more than one axial mode might complicate the situation. Moreover the limited voltage applicability to the phase modulator (Lasermetrics 1039) allows a maximum frequency switch of ~1 GHz.
[24]J. H. Meyling, P. J. Bounds, and R. W. Munn, Chem. Phys. Lett. 51, 234 (1977).
[25]S. I. Weissman and S. S. Kim (to be published).
[26]H. de Vries and D. A. Wiersma (to be published).
[27]J. Wessel, thesis, University of Chicago, 1970.
[28]M. Stockburger, H. Gattermann, and W. Klusmann, J. Chem. Phys. 63, 4529 (1975).
[29]U. Boesl, H. J. Neusser, and E. W. Schlag, Chem. Phys. Lett. 31, 1 (1975).
[30]H. Sixl and M. Schwoerer, Z. Naturforsch. Teil A 25, 1383 (1970).
[31]R. L. Barger, M. S. Sorem, and J. L. Hall, Appl. Phys. Lett. 22, 573 (1973).
[32]R. L. Barger, J. B. West, and T. C. English, Appl. Phys. Lett. 27, 31 (1975).